

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Treatment of Cellulosic Textile Materials

We, HEBERLEIN & Co. A.G., a Swiss Body Corporate, of Wattwil, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the treatment of cellulosic textile materials, and is particularly concerned with the finishing of cellulosic textile materials by treatment with synthetic resin precondensates followed by condensation. By the term "cellulosic textile material" as used herein is to be understood cellulosic textile material of all kinds including textile yarns, fibres, filaments, threads, woven, knitted or non-woven fabrics made of or containing natural cellulose e.g. cotton, regenerated cellulose or cellulose derivatives e.g. cellulose acetate. The term includes for example textile materials made in part from cellulosic fibres and in part from fibres of other natural or synthetic substances.

One process for the resin-finishing of cellulosic textile material is known in which a resin precondensate and a suitable catalyst are applied to the textile material and then condensed by the action of heat. Also, a second process for the resin-finishing of textile material is known according to which a solution of a polymerisable synthetic resin together with an appropriate catalyst is applied to the textile material which is pre-dried at a temperature below the condensation temperature of the resin; ready-made garments are manufactured from the thus treated textile material (changes of shape, e.g. pleats, being provided if desired) and the synthetic resin is then polymerised by heating to temperatures above 100°C. Such a working method has become

known in the textile industry as "deferred curing".

It is furthermore known to react resin precondensates with cellulosic textile material by means of the action of sulphuric acid, for example using strongly acid precondensate baths. Relatively low acid concentrations and longer treatment times in the acidified precondensate bath are in general used, and the treatment is followed by a subsequent retention process. Using a one-bath treatment and the subsequent retention process, a product is directly obtained in which the resin is present in its finished and completely condensed form.

An object of the present invention is to provide an alternative method of finishing cellulosic textile materials which provides a material in an intermediate stage having a high wet crease angle which can be shaped or made up as desired, and which enables finishing to be completed after shaping or making up to give a final product having besides the high wet crease angle also a high dry crease angle.

According to the present invention there is provided a process for the treatment of cellulosic textile material as herein defined which comprises (1) applying to the textile material an aqueous composition containing a synthetic resin precondensate capable of condensing under acid conditions to effect cross-linking of the textile material, (2) drying the textile material at a temperature below the condensation temperature of the precondensate, and (3) treating the textile material with aqueous sulphuric acid at a concentration and for a time whereby partial condensation is effected bonding a number of reactive groups of the resin to the textile material whilst leaving a substantial number of free reactive groups of the precondensate in an unreacted state. The

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finishing of the textile material can then be completed, for example by the steps of (4) shaping or making up the textile material, and (5) heating the textile material in the presence of a condensation catalyst whereby condensation is substantially completed.

In step (4) of the process the textile material can for example be made up into ready-made garments. The condensation catalyst which is necessary in step (5) of the process can if desired be applied to the textile material after step (3) but before step (4) of the process. In this case, step (5) can then be carried out after step (4) by heating alone, for example using an ironing press.

The resin precondensate is bonded to the cellulosic textile material by the action of the sulphuric acid in step (3) of the process; this is shown *inter alia* by the fact that the resin cannot then be removed by washing. Moreover, a cotton fabric for example has a very high wet crease angle after subjection to steps (1) to (3) of the process according to the invention.

Sufficient free reactive groups of the resin precondensate remain after step (3) of the process according to the invention to allow subsequent complete condensation of the resin by a simple heating in the presence of a condensation catalyst with a simultaneous increase of the dry crease angle. The process according to the invention does thus not lead directly to the finished end product but first to an intermediate product in which the resin is present in bonded state but has still sufficient free reactive groups so as to be completely condensed in later reaction step (5). This means that the textile material between steps (3) and (5) of the process according to the invention can if desired be made up or shaped e.g. by forming pleats therein. In the latter case, the pleats can then be fixed by means of step (5) of the process according to the invention.

Suitable resin pre-condensates for use in the process according to the invention include for example precondensates of formaldehyde and a nitrogenous compound. Examples of suitable nitrogenous compounds include for example urea and thiourea and derivatives thereof in particular cyclic ureas having 5- or 6-membered heterocyclic ring systems, bicyclic compounds such as the so-called acetylene diurea, carbamates, and triazine derivatives (such as particularly melamine derivatives).

The process according to the invention can for example be carried out as follows:

The resin precondensate is applied to the fabric in a quantity such as is usual in conventional resin-finishing, preferably by padding. The textile material is then dried. In the following step, the textile material is brought into contact with an aqueous sulphuric acid bath containing between 40 and 60% by weight of sulphuric acid. The treatment

time is conveniently 0.5 to 30 minutes, preferably 1—5 minutes, which, if desired, makes continuous working possible. The sulphuric acid is then completely washed out and the textile material dried. In this condition the resin is already fixed to the cellulose in the sense that it is not removed by washing but it must be assumed that for a substantial part it is bonded unilaterally since sufficient reactive groups still remain to permit a later complete condensation with consequent cross-linking. After this reaction step the textile material can be passed on for further processing or for the manufacture of ready-made clothes. For the final condensation, a condensation catalyst is applied to the textile material. This can be effected by padding or by spraying. As condensation catalysts, the potentially acid-reacting catalysts conventionally used for the hardening of resins are conveniently used. Particularly suitable are salts which at room temperature react neutral but which react acid at the hardening temperature of 120—180°C. Examples of such salts include  $MgCl_2$ ,  $NH_4Cl$ ,  $(NH_4)_2H_2PO_4$ ,  $ZnCl_2$  and  $Zn(NO_3)_2$ . The resin is then completely condensed by heat treatment at 120—180°C. for 1 to 10 minutes. If prior to the heat treatment any changes of shape, such as pleats or pleatings, have been imparted to the textile material, these are fixed permanently whilst the base material is finished so as to be crease-free and smooth drying.

According to one feature of the present invention, step (5) of the process according to the invention is carried out in the presence of a small quantity of at least one compound capable of reacting under acid conditions with the cellulose of the textile material, or with itself and the cellulose of the textile material, whereby the dry crease resistance of the textile material thereby obtained is still further improved. Suitable compounds which under acid conditions react with the cellulose or with themselves and the cellulose and cross-link the cellulose include for example acetals, epoxides, polyepoxides, halohydrins and methylol compounds, i.e. precondensates of formaldehyde and a compound with exchangeable hydrogen atoms, such as for example the methylol compounds of ketones and of urea and thiourea and their derivatives. Particularly useful are precondensates of formaldehyde with cyclic urea derivatives having a 5- or 6-membered heterocyclic ring system and their hydroxy or oxo derivatives, bicyclic heterocompounds such as the so-called acetylene diurea, dicyandiamide, guanidine and carbamates, as well as with triazine derivatives (particularly melamine derivatives), and etherification products thereof. Commercial mixtures of precondensates known for textile finishing can conveniently be used if so desired.

The following examples illustrate the invention:—

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## EXAMPLE 1:

5 A cotton poplin fabric is padded with a solution of 140 g. per litre of "Lyofix CH"—registered Trade Mark (a melamine/formaldehyde precondensate of Ciba, Basle, Switzerland) in water and dried. The fabric is then immersed in a bath of aqueous sulphuric acid (57% by weight  $\text{H}_2\text{SO}_4$ ) for 3 minutes, neutralised with dilute caustic soda solution and rinsed. After a time interval of any desired length, an aqueous solution of "Katalysator PR" (a hardening catalyst of Ciba, Basle, Switzerland) is sprayed on in such a manner that from 1.0 to 1.5 g. of the catalyst is applied to the fabric as uniformly as possible. Drying is then if necessary effected at a temperature below  $100^\circ\text{C}$ . to a moisture content of 10–12%. The fabric is now made up into garments and smoothed, creases being applied as desired. Condensation is then effected at  $150^\circ\text{C}$  for 5 minutes. The thus treated fabrics have a smooth-drying finish and the creases are wash-fixed.

acts on the garments at a temperature of  $160$  to  $170^\circ\text{C}$  for about 5 minutes.

## EXAMPLE 4

65 A cotton fabric is padded with 150 g./litre solution of "Fixapret CP"—registered Trade Mark (dimethylol-dihydroxy-ethylene urea of Badische Anilin & Sodafabrik AG, Ludwigshafen) in water and dried. This precondensate is pre-fixed by treatment for 8 minutes in an aqueous sulphuric acid bath (55% by weight  $\text{H}_2\text{SO}_4$ ). After thorough washing and intermediate drying, the material is padded with an aqueous solution consisting of 75 g. per litre of "Fixapret PH" (dimethylol-propylene urea of Badische Anilin & Sodafabrik AG, Ludwigshafen) and 7.5 g. per litre of  $\text{Zn}(\text{NO}_3)_2$  and dried to 15% of residual moisture. This fabric is worked up to garments, in which pressed-in pleats are permanently fixed by a subsequent heat treatment for 6 minutes at  $140^\circ\text{C}$ . Improved crease angles are at the same time achieved.

## EXAMPLE 2:

25 A cotton poplin fabric is padded with a solution of 1,3-dimethylol-4,5-dihydroxy-ethylene-urea in water. The concentration of the solution and the squeezing of the pads are such that about 5% (calculated on the dry weight of the fabric) of the precondensate is applied to the fabric. After drying the material is treated with an aqueous sulphuric acid solution (57% by weight  $\text{H}_2\text{SO}_4$ ) for three minutes and immediately afterwards is rinsed thoroughly. At any later time the fabric is padded with a catalyst solution consisting of 15 g. of  $\text{Mg Cl}_2 \cdot 6 \text{H}_2\text{O}$  in a litre of water and thereafter dried to a moisture content of 8 to 10%. Subsequently thereto the treated fabric is shaped into garment articles and/or pleated and creased by ironing and is then condensed for 5 minutes at  $145$ – $150^\circ\text{C}$  to wash-fix and improve the crease resistance of the base pieces of the product.

85 An imitation linen spun viscose rayon fabric is padded with a solution of 150 g./litre of a commercial tetramethylol-acetylene diurea resin in water and dried. For pre-fixing this resin, the fabric is placed into an aqueous sulphuric acid bath (52% by weight  $\text{H}_2\text{SO}_4$ ) for 2 minutes. It is then thoroughly rinsed and dried. In combination with the later working up into garments, an aqueous solution containing a mixture of a propylene urea-formaldehyde precondensate and magnesium chloride in a weight ratio of 5:2 is sprayed on until 1.4% (calculated on the weight of the fabric) of magnesium chloride are applied. After the working up into garments and the optional pressing in of pleats, the condensation is completed by heating to  $125$ – $130^\circ\text{C}$  for 10 minutes, whereby the pressed-in pleats are fixed with a simultaneous improvement of the crease resistance of the fabric.

## EXAMPLE 3:

45 A cotton fabric is padded with a solution of 300 g./litre of dimethylol methyl carbamate (50%) in water and dried. It is then brought into contact with aqueous dilute sulphuric acid (54% by weight  $\text{H}_2\text{SO}_4$ ) for 10 minutes. The sulphuric acid is then completely washed out by first neutralising and then thorough rinsing. The material is then padded with a solution consisting of 10 g./litre of zinc nitrate and 30 g./litre of an about 50% commercial ethylene urea formaldehyde precondensate and again dried. Fabrics thus pre-treated are worked up to garments, to which pleats are applied as desired. The pleats are fixed (i.e. to be resistant to washing) as well as an improved crease resistance achieved, using an ironing press which

## EXAMPLE 6

110 A mixed fabric consisting of 65% by weight of cotton and 35% by weight of polyester staple fibres is padded with 140 g./litre of a precondensate which has previously been prepared according to known methods from urea and glyoxal and by methylation. The fabric is then dried. It is pre-fixed by treatment for 3 minutes in an aqueous sulphuric acid bath with a  $\text{H}_2\text{SO}_4$ -content of 56% by weight; it is then washed neutral. After an intermediate drying, the fabric is pulled through an aqueous solution consisting of 80 g./litre of ethylene urea formaldehyde precondensate (50%) and 8 g./litre of  $\text{Zn}(\text{NO}_3)_2$  and is then squeezed off to 65%. It is then dried to a residual moisture content of about 12%. The fabric is ready at this stage to be worked up into garments. If intentional

creases are here applied, an end treatment by heating to 150°C for 5 minutes is sufficient in order to fix the material wash-resistant, with a simultaneous improvement of the dry crease angle; the wet crease angle is already substantially increased after the process step (3) in the sulphuric acid bath.

# WHAT WE CLAIM IS:—

1. A process for the treatment of cellulosic textile material as herein defined which comprises (1) applying to the textile material an aqueous composition containing a synthetic resin precondensate capable of condensing under acid conditions to effect cross-linking of the textile material, (2) drying the textile material at a temperature below the condensation temperature of the precondensate, and (3) treating the textile material with aqueous sulphuric acid at a concentration and for a time whereby partial condensation is effected bonding a number of reactive groups of the resin to the textile material whilst leaving a substantial number of free reactive groups of the precondensate in an unreacted state.

2. A process according to claim 1 in which the synthetic resin precondensate is a precondensate of formaldehyde and a nitrogen-containing compound.

3. A process according to claim 2 in which the nitrogen-containing compound comprises a cyclic urea having a 5- or 6-membered heterocyclic ring system.

4. A process according to claim 2 in which the nitrogen-containing compound comprises a carbamate.

5. A process according to claim 2 in which the nitrogen-containing compound comprises a triazine compound.

6. A process according to any of the preceding claims in which the synthetic resin precondensate is applied to the textile material by padding.

7. A process according to any of the preceding claims in which in step (3) the textile material is immersed in a 40 to 60% by weight aqueous solution of sulphuric acid.

8. A process according to claim 7 in which the immersion time is from 0.5 to 30 minutes.

9. A process according to claim 8 in which the immersion time is from 1 to 5 minutes.

10. A process according to any of the preceding claims in which after step (3) the textile material is washed with a neutralising solution.

11. A process according to claim 10 in which the neutralising solution comprises a dilute caustic soda solution.

12. A process according to any of the preceding claims in which, after step (3), the textile material is subjected to the steps of (4) shaping or making up the textile material, and (5) heating the textile material in the presence of a condensation catalyst whereby condensation is substantially completed.

13. A process according to claim 12 in which in step (5) the textile material is heated to a temperature of from 120 to 180°C to effect complete condensation.

14. A process according to claim 13 in which the condensation catalyst is a compound neutral at room temperature but acid at 120 to 180°C.

15. A process according to any of claims 12 to 14 in which the condensation catalyst comprises magnesium chloride.

16. A process according to any of claims 12 to 14 in which the condensation catalyst comprises ammonium chloride, ammonium dihydrogen orthophosphate, zinc chloride or zinc nitrate.

17. A process according to any of claims 12 to 16 in which the condensation catalyst is applied to the textile material after step (3) and before step (4).

18. A process according to any of claims 12 to 17 in which the condensation catalyst is applied by padding.

19. A process according to any of claims 12 to 17 in which the condensation catalyst is applied by spraying.

20. A process according to any of claims 12 to 19 in which in step (5) heating is effected for from 1 to 10 minutes.

21. A process according to any of claims 12 to 20 in which step (5) is carried out in the presence of a small quantity of a compound capable of reacting under acid conditions with the cellulose of the textile material, or with itself and the cellulose of the textile material, whereby the dry crease resistance of the textile material thereby obtained is improved.

22. A process according to claim 21 in which the said compound comprises a precondensate of formaldehyde and a compound with exchangeable hydrogen atoms.

23. A process according to claim 22 in which the compound with exchangeable hydrogen atoms comprises a cyclic urea having a 5- or 6-membered heterocyclic ring system.

24. A process according to any of claims 21 to 23 in which the compound capable of reacting with the cellulose, or with itself and the cellulose, is substantially as herein described.

25. A process according to any of the preceding claims in which the cellulosic material comprises natural cellulose.

26. A process according to claim 25 in which the textile material comprises cotton.

27. A process according to any of claims 1 to 24 in which the textile material comprises regenerated cellulose.

28. A process according to claim 1 or claim 12 substantially as herein described.

29. A process according to claim 12 substantially as herein described in either of Examples 1 and 2.

30. A process according to claim 12 sub-

stantially as herein described in any of Examples 3 to 6.

31. A cellulosic textile material when treated by a process as claimed in any of  
5 claims 21 to 28 and 30.

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